

Transient Absorption Spectroscopy of TlBr Crystals Using Pulsed Electron Beams

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We analyzed the transient absorption properties of TlBr crystals using pulsed electron beams as excitation sources. We observed transient absorption spectra and temporal profiles on the pico- and nanosecond scales and compared the results obtained for TlBr crystals that are empirically *appropriate* with those that are *inappropriate* for semiconductor detectors. The results showed negligible differences in properties between the two types of crystal, which indicates that their trap center concentrations were similar. A transient absorption band was observed at approximately 1160 nm on the nanosecond scale, while its short-wavelength tail was observed on the picosecond scale. The absorption band is attributed to the localized holes at Tl^+ that are stabilized by some defects. In contrast, no absorption band attributable to localized electron centers was observed, indicating that while hole transport is hindered by defects, electron transport is not.

1. Introduction

TlBr is an indirect-gap semiconductor with direct and indirect gap energies of approximately 3.0 and 2.7 eV, respectively.^(1–5) Owing to the high atomic numbers of its constituent elements (Tl: 81, Br: 35) and the consequent high interaction probability with high-energy photons such as X-rays and gamma rays, TlBr has long been a candidate material for semiconductor detectors of ionizing radiations.⁽⁶⁾ Its relatively high band-gap energy is also favorable for use at room temperature. Semiconductor detector applications require single crystals of high purity and quality to obtain an excellent energy resolution. However, the development of such applications is limited by issues such as crystal growth reproducibility.

Thus far, TlBr crystal quality has been evaluated using many analysis methods. Among them, optical characterizations have been extensively studied. For instance, the band structure

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and exciton properties have been investigated using electroabsorption⁽⁷⁾ or electroreflectance spectroscopy.⁽⁸⁾ Photoconductivity studies have revealed the transport properties of the optically produced electron–hole pairs.^(9–12) Similarly, photoluminescence, cathodoluminescence, and scintillation spectroscopies with steady-state and time-resolved measurements at different temperatures have revealed lattice imperfections such as point defects and dislocations.^(13–16)

In this study, we employed transient absorption spectroscopy to characterize TlBr crystals. This is a powerful technique to analyze the dynamics of electron–hole pairs. In a previous study,⁽¹⁴⁾ transient absorption spectra were recorded after 20 ns of excitation using a pulsed electron beam. In this study, we recorded the transient absorption on the pico- and nanosecond scales and compared the transient absorption characteristics of the crystals that are empirically known to be *appropriate* for semiconductor detectors with those of crystals known to be *inappropriate*.

2. Materials and Methods

TlBr crystals were grown from raw TlBr powder (Sigma-Aldrich, 99.999%) after many runs of purification by the travelling molten zone (TMZ) method. We used two types of crystal: the first was obtained from a portion of a crystal boule that is empirically known to be *appropriate* for semiconductor detectors. This crystal was grown after 322 runs of purification by the TMZ method. The second was obtained from a portion of a crystal boule that is empirically known to be *inappropriate* for semiconductor detectors. This crystal was grown after 228 runs of purification by the TMZ method. The crystals were obtained from the same portion as those used in our previous study.⁽¹³⁾ The thicknesses of the *appropriate* and *inappropriate* crystals were 0.611 and 0.616 mm, respectively. The details of the crystal growth have been described in a previous paper.⁽⁶⁾ After the crystal growth was completed, all measurements were performed at room temperature in air.

The transient absorption after pulsed beam irradiation in the picosecond scale was observed using a measurement system at the Nuclear Professional School, School of Engineering, The University of Tokyo. The crystals were irradiated with a pulsed electron beam whose energy, pulse duration, and charge were 22 MeV, 7 ps at full width at half maximum, and 2.5 nC, respectively. The transient absorption spectra were recorded using white light pulses as the probe light, which were obtained by focusing the fundamental light (780 nm and 100 fs) of a Ti-sapphire laser (Coherent Inc., Libra-F-HE) onto a CaF₂ single crystal. The intense fundamental light in the probe light was cutoff using a band-stop filter prior to its incidence on the sample. The transmitted light spectra of the samples with and without pulsed electron beam irradiation were measured using a photonic multichannel analyzer (Hamamatsu, PMA-20) to obtain the transient absorption spectra. The incident time of the probe light pulses was controlled using an optical delay line up to 40 cm, which corresponds to the time scan width of 2.6 ns. The signal-to-noise ratio (S/N) was relatively low, below 450 nm, owing to the low intensity of the transmitted light. The details of the measurement system were described in a previous paper.⁽¹⁷⁾

The transient absorption after pulsed electron beam irradiation on the nanosecond time scale was measured using a measurement system at The Institute of Scientific and Industrial Research, Osaka University. The samples were simultaneously irradiated with the pulsed electron beam and a pulsed probe light from a flash lamp (Takasago Ltd., YAMA-1500). The energy, duration, and charge of the electron beam were 28 MeV, ~ 8 ns, and 90 nC, respectively. The duration of the pulsed light was several tens of microseconds, which was much longer than that of the pulsed electron beam. Thus, the pulsed light can be considered as a quasi-continuous light. The transmitted light was monochromatized using monochromators for UV-to-visible (UV-VIS; <900 nm) and IR (>900 nm) wavelength regions; the light in each region was detected using a Si photodiode and an InGaAs photodiode, respectively. A digital oscilloscope (Tektronix Inc., DPO7254) was used to record the output signals in the form of transmitted light intensity as a function of time. Transient absorption temporal profiles were obtained as the difference in the transmitted light intensity as a function of time between samples with and without pulsed electron beam irradiation; these profiles at different wavelengths were then used to obtain the transient absorption spectra. The S/N was relatively low, below 450 nm, owing to the low intensity of the transmitted light. A small peak at approximately 150 ns corresponds to the reflection noise. The details of the measurement system have been reported elsewhere.^(18,19)

3. Results

Figure 1 shows the time-resolved transient absorption spectra of the *appropriate* and *inappropriate* crystals on the picosecond scale. We observe the short-wavelength edge of the spectra of approximately 430 nm, whose photon energy is between the indirect and direct bandgap energies of approximately 2.7 and 3.0 eV, respectively. The photon energy of the short-wavelength edge is higher than the indirect bandgap energy owing to the low absorption coefficient for the optical transition at the indirect gap. The blank wavelength region between 767 and 804 nm corresponds to the band-stop filter that suppresses the fundamental light of the Ti-sapphire laser. Furthermore, we observe that the spectra are not composed of absorption

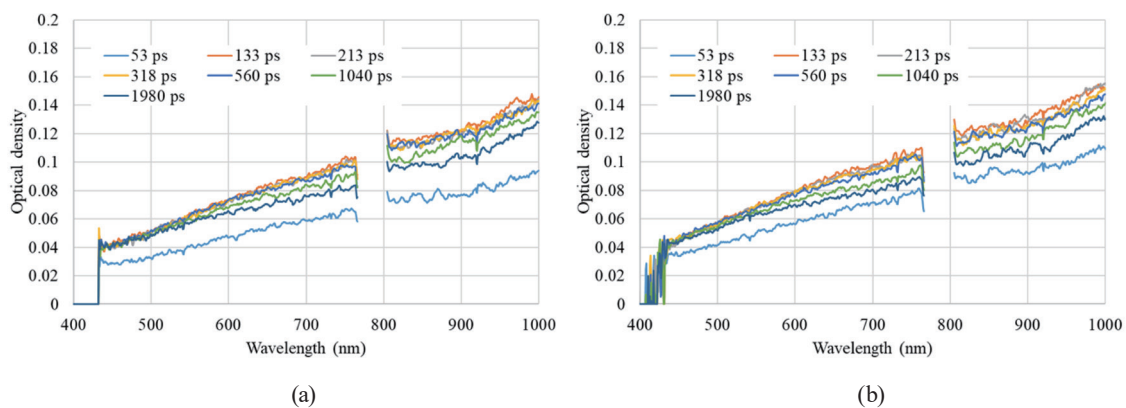


Fig. 1. (Color online) Time-resolved transient absorption spectra of (a) *appropriate* and (b) *inappropriate* crystals on the picosecond scale.

bands and also do not exhibit an emission band; they are represented by a straight line having a positive slope with wavelength. Figure 2 shows the transient absorption temporal profiles of the *appropriate* and *inappropriate* crystals on the picosecond scale. We observe a steep rise within 70 ps, although slightly slower than the time resolution of the measurement system at ~ 25 ps. After this rise, the optical density slightly decreases within the time window of ~ 2 ns; this decrease is more significant for longer wavelengths. The transient absorption spectra in Fig. 1 indicate that the slope becomes gentler over time.

Figure 3 shows the transient absorption spectra of the *appropriate* and *inappropriate* crystals on the nanosecond scale. We observe that the spectra at 10 ns has a complicated shape because of significant noise, while that at 20 ns and later have a simple structure with a peak at approximately 1160 nm. Figure 4 shows the transient absorption temporal profiles of the *appropriate* and *inappropriate* crystals on the nanosecond scale. We observe no significant difference in the decay behavior at different wavelengths, except for the initial slower decay at 1100 nm. Moreover, the decay behavior has not been expressed with a single exponential decay or $1/t$ dependence, which is generally applied to the decay kinetics of the second order.

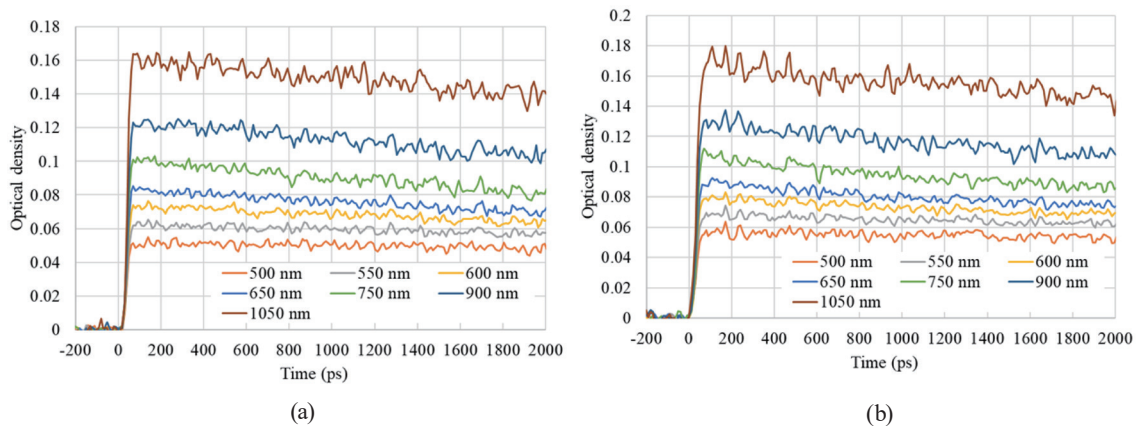


Fig. 2. (Color online) Transient absorption temporal profiles of (a) *appropriate* and (b) *inappropriate* crystals on picosecond scale.

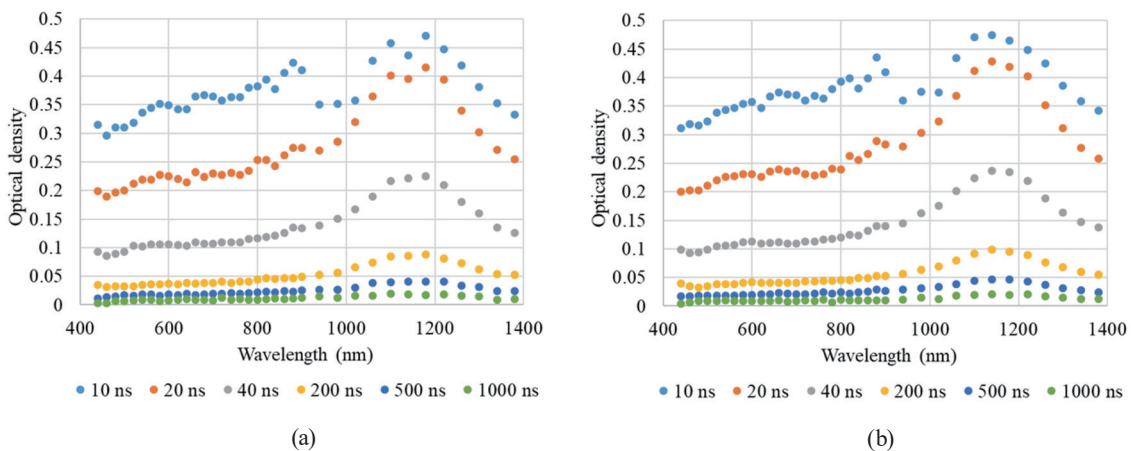


Fig. 3. (Color online) Time-resolved transient absorption spectra of (a) *appropriate* and (b) *inappropriate* crystals on nanosecond scale.

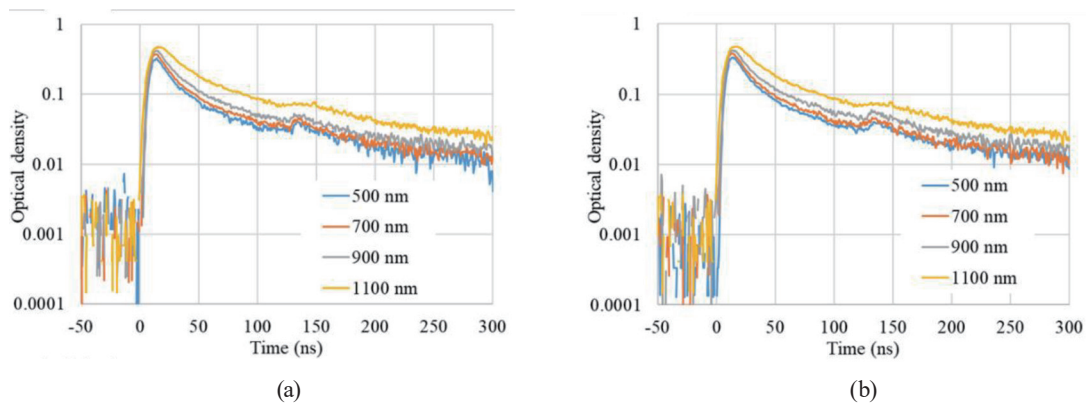


Fig. 4. (Color online) Transient absorption temporal profiles of (a) *appropriate* and (b) *inappropriate* crystals on the nanosecond scale.

4. Discussion

The transient absorption spectra at 20 ns and later have a broad peak at 1160 nm with a somewhat broad tail toward the short wavelength side down to ~ 450 nm. Besides, this peak wavelength (i.e., 1160 nm) is outside the wavelength range of the picosecond measurements. We observe that the slope of the transient absorption spectra on the picosecond scale exhibits a nearly linear dependence on the wavelength λ . This dependence contradicts the dependences of free-carrier absorption, which exhibit a wavelength dependence of $\lambda^{1.5}$, λ^2 , $\lambda^{2.5}$, or $\lambda^{3.5}$, based on the scattering mechanism.^(20,21) Moreover, because no absorption band is observed below 1000 nm both on the pico- and nanosecond time scales, we can safely conclude that the transient absorption spectra on the picosecond scale up to 1000 nm represent the tail of the absorption band at 1160 nm. A previous paper has already shown the transient absorption band at 1160 nm, which is attributed to holes at the TI site (Ti^{2+}) stabilized by some defects.⁽¹⁴⁾ The observation of this peak strongly suggests that some hole traps suppress the hole transport in these crystals. However, unlike the crystals reported in the previous paper,⁽¹⁴⁾ no absorption band at ~ 2.2 eV, which is attributed to electron-trapping centers, was observed in the present study. These results indicate that the hole transport of the crystals can be improved by suppressing the generation of related defects, and the electron transport properties of the present crystals are significantly better than those of the crystals analyzed in the previous paper.⁽¹⁴⁾

Considering the dynamics, the steep rise in the transient absorption temporal profiles within 70 ps indicates that some holes are trapped after the production of the electron–hole pairs in less than 70 ps. The decay on the picosecond scale was negligible, which indicates that the electron–hole recombination is negligible in this time scale. Furthermore, the decay behavior on the nanosecond scale is not represented by a single exponential decay function nor a $1/t$ dependence, which indicates that the decay behavior cannot be described by either the first-order kinetics having a single decay channel or second-order kinetics. Therefore, these results strongly suggest that the decay can be expressed with a sum of multiple exponential decay functions, which corresponds to multiple decay channels. Hence, a plausible origin of the

multiple decay channels is hole traps of several types. Besides, the decay time scale indicates that the hole traps hinder the hole transport.

The difference between transient absorption behaviors on the pico- and nanosecond scales of the *appropriate* and *inappropriate* crystals was negligible, which suggests that the electron and hole trapping behaviors of the crystals are almost similar, although the crystals exhibited significant differences in their photoluminescence and radioluminescence spectra in our previous paper,⁽¹³⁾ in which it is strongly suggested that the concentration of dislocation-type defects was significantly different between the two crystals. These results indicate that the two crystals were similar from the viewpoint of the concentration of point defects, whereas they are quite different in the dislocation concentration. As a future prospect, similar measurements under operation as semiconductor detectors would give useful information on the carrier transport.

5. Conclusions

We analyzed the transient absorption spectra of TlBr crystals using pulsed electron beam irradiation and obtained their temporal profiles on the pico- and nanosecond scales. On the basis of the spectral shape on the nanosecond scale, the transient absorption is attributed to the localized holes at Tl^+ stabilized by some defects. Unlike the previously reported transient absorption,⁽¹⁴⁾ no absorption band of localized electron centers at 2.2 eV was observed in this study. These results indicate that while some defects hinder the hole transport, the electron transport is not hindered by the defects. Moreover, a negligible difference in transient absorption behavior was observed between the *appropriate* and *inappropriate* crystals, which indicates that the defect concentrations of electrons and hole-trapping centers are similar.

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